



Keywords:
Wood protection
Treatments
Nanostructures
Nanotechnology
Biocides

Historic:
Received 05/03/2018
Accepted 08/11/2018

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NANOPARTICLES-BASED WOOD PRESERVATIVES: THE NEXT GENERATION OF WOOD PROTECTION?

BORGES, C. C.; TONOLI, G. H. D.; CRUZ, T. M.; DUARTE, P. J.; JUNQUEIRA, T. A. Nanoparticles-based wood preservatives: the next generation of wood protection?. **CERNE**, v. 24, n. 4, p. 397-407, 2018.

HIGHLIGHTS

Review on biocides nanoparticles.

Nanoparticles-based wood preservatives.

Nanoparticles biocides applied on wood protection.

Protection against biodeterioration through nanotechnology.

ABSTRACT

Wood is a natural material that presents a great variation of properties. Many treatments have been developed in order to extend the service life of wood products. Nowadays, products with low toxicity and economic viability are a challenge to researchers. Nanotechnology has been indicated as a solution to this issue, since wood preservatives can be utilized in low concentration, promoting satisfactory results in terms of protection with no color changes. The main goal of this review is to present nanotechnology advances on wood protection. Self-cleaning surfaces, scratch and weathering resistance, and biocides properties have been achieved through nanoparticles (NPs) applications. Studies evaluating the performance of NPs from silver (Ag), boron (B), copper (Cu), zinc (Zn), zinc oxide (ZnO), zinc borate ($B_2O_6Zn_3$), and titanium dioxide (TiO_2) on wood protections have reported promising findings. Tests performed against termites, rot, mold and stain fungi, and UV degradation have demonstrated that some biocides have their properties improved in nanoscale. Controlled release and encapsulation technologies are another important matter once it can increase the effectiveness of wood treatments. NPs risk assessment for human health and the environment are still incipient. Despite of that, some products as nanozinc oxide (nanoZnO) and titanium dioxide (nanoTiO₂) present encouraging potential. NanoZnO and NanoTiO₂ have been reported as promising antifungals, antibacterials, and antiviral agents; beyond their biocides properties, low ecotoxicity impacts to the environment are expected. Based on this review, we consider that wood treatments based on NPs may play an important role in the next generation of wood protection systems.

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INTRODUCTION

Solid wood is a naturally created polymer composite, that results of the combination of cellulose, hemicelluloses and lignin naturally arranged into tubular structures that eventually forms a cylindrically layered composite (Csanády et al., 2015). Wood is a renewable material that has sustainable credentials. According to Food and Agriculture Organization of the United States (FAO, 2016), greater wood use can make a significant contribution to society's desire for a more sustainable future. Using wood reduces carbon emissions, due to carbon dioxide stored in the timber products. Nowadays, carbon credits are traded as part of a voluntary market in the U.S., while Europe, which ratified the Kyoto Protocol, has a regulated carbon market (Ryan et al., 2010).

Timber has high strength to weight ratio, and is used efficiently in structures where it is carrying a lot of its own self-weight (Ramage et al., 2017). Since the earliest days of human civilization, wood has been a valuable and effective structural material for construction. However, lumber is not naturally durable, and to ensure durability it is necessary to make it resistant through treatments (Canadian Wood Council, 2018). Durability assessment is only based on the tree's heartwood, and not on its sapwood. Due to its extractives, heartwood, has any appreciable degree of durability, while sapwood should be considered perishable.

Nowadays, lumber has been treated with preservatives in order to increase durability. However, there is increasing pressure to be environmentally friendly and to reduce, restrict, or eliminate the use of wood preservatives because of the concern that toxic constituents may leach from the treated wood (Groenier and Lebow, 2006). Conventional wood preservatives such as chromated copper arsenate (CCA), chromated copper borate (CCB), are very effective to protect wood, however cause environmental pollution and some of them are hazardous to animals and human being (Venmalar, 2017). Due to the presence of arsenic, wood treatments based on CCA increase the environmental impacts and have limited commercialization, proving the necessity of development of new products for wood preservation (Santos et al., 2012).

In Brazil, traditional treatments based on CCA and CCB are the most utilized (Vidal et al., 2015); even if this kind of treatment causes undesirable wood color changing, and presents risks to environment and human health, they have a significantly higher performance than alternative copper-based preservatives. It has been shown that the percentage of copper removed during leaching

tests was higher from wood treated with alternative copper-based preservatives than that of CCA treated wood (Temiz et al., 2014). For retentions of CCA-C greater than $6.8 \text{ Kg}\cdot\text{m}^{-3}$ the expected lifetimes are over 50 years (Jankowsky et al., 2012). Since increasing life of a wood product implies less work related to replacement and lower cost for the user, this kind of treatment can give a positive environmental contribution because of the extended time of storage of carbon in each wood product, and the longer time to replacements, because every replacement results in an environmental impact (Alfredsen et al., 2017).

However, the Environment Protection Agency (EPA) of United States is reevaluating all chromated arsenical products as part of the Registration Review program (2015) to ensure chemicals can perform their function without adverse effects on human health or environment. CCA has been voluntarily phased out for most uses around residential areas and other areas where human contact with preservative-treated wood is common (Groenier and Lebow, 2006). Thus, the searching for new treatments with efficiency, low toxicity, no danger to human health, and viability of costs production is a challenge for researchers on wood protection.

In this context, nanotechnology advance should be a key for the future of wood protection sciences, since NPs present the possibility of low concentration usage, maintaining the natural color of the wood and controlled releasing of the active ingredient. The main goal of this review is to present advances and possibilities of nanotechnology application on wood protection.

WOOD PROTECTION

Some species of wood have natural resistance to decomposition caused by microorganisms and insects, however, many of them are scarce or do not grow fast enough to attend the market's demand (Lebow, 2010). Natural resistance happens due extractives that are substances formed on the tree, and naturally deposited into heartwood. Besides protection, extractives are responsible for the color of the heartwood, the wood part that presents natural durability (Lepage et al., 2017). In general, heartwood from some species is durable (Richardson, 2002), while sapwood from all species is very susceptible to decay (Lepage et al., 2017). Species with darker colored or denser woods are most durable, with high natural resistance. But, indeed, there is no wood that possesses natural resistance to all biodeterioration agents (Richardson, 2002).

Wood protection is a solution to this impasse. Wood protection science is the process of addition of toxic or repellent substances called preservatives into wood, in order to increase resistance to decay and durability (Lepage et al., 2017). Preservative treatments can increase wood service life, reducing replacement costs and allowing efficient use of forest resources. Through them, wood products can be protected against several attacks, as decay fungi, harmful insects, or marine borers (Lebow, 2010).

Regardless of the treatment received, some wood protection requirements have to be attended. To obtain long-term effectiveness, adequate penetration and retention are required for each wood species, chemical preservative, and treatment method. The degree of protection achieved depends on the product used and the proper penetration and retention of the chemicals, according to efficacy and adaptability to the use requirements (Lebow, 2010).

Leaching also affects the efficacy of the treatment, as well as, the potential impacts on human health and the environment. In the risk assessment of wood preservatives, it is important to know the preservative leaching rates under different exposure scenarios (Waldron et al., 2004).

Considering nanotechnology approaches, the releasing of wood preservatives is another important question. Encapsulation technologies and controlled release methods have revolutionized the use of pesticides and herbicide (Joseph and Morrison, 2006) and may do the same to the wood protection in the near future.

Nowadays, several studies present applications of nanotechnologies on wood protection. In the next sections, they will be properly discussed, looking for high efficiency, low risks to human health, and environmental sustainability.

WOOD PRESERVATIVES

Structure of cell membranes and DNA (deoxyribonucleic acid) have specific and crucial metal ions; half of that known proteins are predicted to be dependent on metal atoms for their structure and participation in key cellular processes (Waldron and Robinson, 2009; Andreini et al., 2004). In spite of that, these essential metals are lethal to all cells when present in excess, and certain non-essential metal such as Ag, mercury (Hg) and tellurium (Te) are extremely poisonous even at exceptionally low concentrations. Consequently, metals have been used for their antimicrobial properties for thousands of years; they inhibit microbial growth, and

kill microorganisms, and their application have also been prized in agriculture, as well as enjoyed a rich history in medicine (Lemire et al., 2013).

In regard to wood protection, several chemicals called preservatives are traditionally used as biocides. Preservatives have fungicide and insecticide action, and can be applied separated or together, according to the service requirements. Preservatives can also be incorporated to coatings to protect against others kinds of deterioration, as light (UV) degradation, for example.

Wood preservatives can be classified according to the solvent, such as oil-based, solvent-based and water-based preservatives. The main oil-based preservative is creosote, a derived from the distillation of coal tar, with fungicide and insecticide action, that consists of hundreds of compounds and has a variable composition. Solvent-based preservatives include naphthenates (Cu and Zn), fire-retardants (borates), copper-8-quinolinolate (oxine copper), tributyltin oxide (TBTO), 3-Iodo-2-propynyl N-butylcarbamate (IPBC), and isothiazolones (Lepage et al., 2017; Ash and Ash, 2004). Some solvent-based preservatives are prohibited in Brazil, like as pentachlorophenol that is a solvent-based preservative widely used as a pressure-treatment to wood in the United States (United States Department of Agriculture – USDA, 2018).

Water-based preservatives include CCA and CCB, alkaline borates, copper azoles B (CA-B), micronized copper azoles (MCA-B and MCA-Q), copper HDO (CXA), and others (Lepage et al., 2017). Ammoniacal copper zinc arsenate (ACZA), alkaline copper quaternary compounds (ACQ), and copper azoles are also water-based preservatives (CBA-A). Some preservatives are no longer available commercially, as acid copper chromate (ACC), ammoniacal copper arsenate (ACA), ammoniacal copper citrate (CC), and copper dimethyldithiocarbamate (CDDC) (USDA, 2018). Besides these, chromated zinc chloride (CZC), ammoniacal copper zinc arsenate (ACZA), and other several chemicals have been developed to control internal decay, and protect wood against surface degradation (Zabel and Morrel, 2012).

Insecticides for curative treatments, as pyrethrins and pyrethroids, neonicotinoids, fipronil, and fungicides as carbendazim; products for pretreatment based on carbendazim and cupper oxine; insecticides for plywood's glue line, as cypermethrin and IPBC; and fumigant as Bromomethane (methyl bromide) and phosphine, as well as, biological products, are all used as preservatives (Lepage et al., 2017).

The evaluation of preservatives performance on wood protection is a slow and expensive process. Field-testing experiments of treated wood is the most reliable to evaluate performance with respect to durability and expected service life (Lepage et al., 2017). Unfortunately, the lack of data, the number of involved factors, and how deterioration affects treated performance, make service life prediction very hard and hypothetical (Van de Kuilen, 2007; Brischke et al. 2011; Lepage et al., 2017).

POTENCIAL OF NANOTECHNOLOGY ON WOOD PROTECTION

Nanotechnology has been described as the design, characterization, development and application of materials, devices and systems by controlling shape and size at the nanoscale. NPs have multiple applications in medicine, industry and commercial products. (Weir et al., 2008).

Nowadays, an increasing amount of consumer goods contains engineered NPs (Massari et al., 2014). Engineered NPs hold great promise for a variety of industrial and consumer applications, due to their properties (Kaiser et al., 2013a; Resch and Farina, 2015). The paint industry expects that nanomaterials improve ink properties such as water repellence, scratch resistance, durability and antimicrobial properties (Kaiser et al., 2013a). Preparation of self-cleaning surfaces and improvements of properties such as scratch and weathering resistance, have been achieved using NPs, which is also associated with antimicrobial properties of materials (Kandelbauer and Widsten, 2009).

NPs are obtained from a wide variety of materials. The most common of the new generation of NPs are ceramics. They are divided into: (1) metal oxide ceramics such as titanium (Ti), Zn, aluminum (Al), and iron (Fe) oxides; and (2) silicate nanoparticles (silicates, or silicon oxides, are also ceramic). Generally, they are in the form of nanoscale flakes (Holister et al., 2003).

Manipulation at the nanometric level can modify properties for new applications in physics, chemistry, biology, and materials science (Resch and Farina, 2015). The transition from microparticles to NPs can change a number of physical properties, because of the increasing in the ratio of surface area to volume, and the quantum effects of the size particle (Holister et al., 2003). Metallic NPs, as photoactive nanoTiO₂ or nanosilica dioxide (nanoSiO₂), may improve paint properties, such as water repellence, scratch resistance, durability and antimicrobial properties (Kaiser, 2013a). According to Liu et al. (2002), biocides can be incorporated into several different polymers, copolymers, and polymer

blends. Due to the innovation potential, market growth, and the benefits related to NPs, nanotechnologies are considered a strategic area (Resch and Farina, 2015).

Fungicides (tebuconazole, chlorothalonil, and KATHON 930) and one insecticide (chlorpyrifos) incorporated into NPs were reported on wood protection with high biological efficacy for all of them (Liu et al., 2002). Nano wires of vanadium pentoxide were identified as having a potential to be an alternative approach to conventional anti biofouling agents (Natalio et al., 2012). Results of combination of cooper oxide NPs (nanoCuO) and fluconazole were reported as a potential treatment against fungi on humans (Weitz et al., 2015).

Performance of wood treated with metallic NPs, based on termite bioassays, was previously reported (Clausen et al., 2009; Kartal et al., 2009; and Mantanis et al., 2014). Treatments performed in southern yellow pine (SYP) with nanoZnO of 30 and 70 nm diluted in water (1.0, 2.5 and 5.0%) presented less than 4% of wood consumption, and caused 94 to 99% of termite mortality after 25 to 27 days incubation. In contrast, termites consumed 10 to 12% of the blocks treated with zinc sulfate (ZnSO₄), and termite mortality was considerably lower for all three ZnSO₄ treatment concentrations, 1.0, 2.5 and 5.0% (Clausen et al., 2009). Lower termite mortality in ZnSO₄ treated wood compared to nanoZnO may be due to differences in bioactivity that results from changes in the chemical structures (Serine et al., 2009). Particles of boron (nanoB) of 30 nm (1%) and boric acid (H₃BO₃) control at 1% caused 100% of termite mortality in SYP, while NanoZn (30 nm) with surfactant (1%) caused moderate termite mortality (31%), and ZnSO₄ at 1% resulted in low mortality rates of 1-7% (Kartal et al., 2009). Treatments with particles of 80 nm (2%) of nanozinc borate (B₂O₆Zn₃) and nanozinc borate plus water-borne acrylic polymer emulsion caused 100% termite mortality in black pine treated wood (*Pinus nigra* L.), with a considerably low mass losses, i.e. 3.3% and 2.3%, respectively. NanoZnO (80nm, at 2%) formulations caused low mortalities at 9-10%, while suffered significantly low mass losses at 4-7% (Mantanis et al., 2014). NanoCuO provides no protection to termites (Kartal et al., 2009; Mantanis et al., 2014).

Attempts of mold growth control using metal NPs were reported in literature by several authors (Kartal et al., 2009; Clausen et al., 2009; Mantanis et al., 2014). Against mould growth, nanometals preparations of 30 nm (Cu, Zn or B at 1%) and respective controls (cooper sulfate (CuSO₄), ZnSO₄, and H₃BO₃ at (1%) and untreated) failed to provide adequate protection to wood (Kartal et al., 2009). However, results of Mantanis et al.

(2014) demonstrate a slightly inhibition of mold fungi by nanozinc borate of 80nm (2%). At high concentration, NanoZnO treatments (30 and 70 nm, at 5%) resulted in moderate inhibition (20 – 32%) of mold and sapstain growth (Clausen et al., 2009). Concerning to nanosilver (nanoAg), it was reported the protective effect against mold, blue stain fungi and algae was insufficient for coatings (Künniger et al., 2013).

NPs (30 nm) of Cu, Zn and B at 1% inhibited the white-rot test fungus *Trametes versicolor* (Kartal et al., 2009). The same white-rot fungi (*Trametes versicolor*) was significantly inhibited by nanoZn-based preparations in different treatments and concentrations (Clausen et al., 2009; Kartal et al., 2009; Mantanis et al., 2014). Nanozinc borate (80 nm, at 2%) plus acrylic emulsion imparted very high resistance in pine wood to the white-rot fungus (Mantanis et al., 2014).

Prevention of decay caused by *Hypocrea lixii* (white-rot) and *Mucor circinelloides* (brown-rot) were reported in *Pinus Sylvestris* L., *Abies alba* M., *Junglas regia* L., *Castanea sativa* M., *Prunus avium* L., *Quercus petrea* L., *Fagus sylvatica* L., and *Fraxinus excelsior* L., independently of wood species and fungus type, through photo-catalytic activity of NanoTiO₂. In that work, TiO₂ impregnation was performed by immersion of untreated samples for seven days in a solution of TiO₂ NPs (0.25 mg/mL) and 0.01 mL of surfactant (De Filpo et al., 2013).

NanoZnO (30 and 70 nm) did not significantly inhibit brown-rot fungi *Postia placenta* (2.5 or 5.0%) or *Antrodia* sp. (1.0%). At 5.0%, nanoZnO caused 74% lower mass losses than in the untreated control in *Gloeophyllum trabeum* attack (Clausen et al., 2009). Copper-treated (30 nm, at 1%) specimens exposed to *Antrodia* sp. showed high mass losses (19 - 33%). However, mass loss of treated wood exposed to *G. trabeum* was greatly reduced (65%) with nanoCu (1%) or CuSO₄ (3–15%), compared with untreated controls (Kartal et al., 2009). SYP treated with KATHON 930 in polyvinylpyridine, at levels of 0.1 Kg of biocide/m³, presented weight loss of only 5% after 50 days of exposure to *G. trabeum* (Liu et al., 2002). NanoZnO (80 nm, at 2%) and nanozinc borate treatments (80 nm, at 2%) did not inhibited the brown-rot fungus *Tyromyces palustris* (Mantanis et al., 2014). Treatments results of basic copper carbonate NPs (CuCO₃·Cu(OH)₂) against the brown rot fungus *Rhodonia placenta* also do not support increasing antifungal efficacy due to nanosizing effects (Civardi et al., 2015a).

NanoZnO particles (30 nm) were reported on wood weatherability control. Graying was significantly reduced by nanoZnO treatments at high concentration

(5%), but it was not completely eliminated (Clausen et al., 2010). It happens because ZnO is a highly effective UV protector, due its strong ultraviolet absorption (Yu et al., 2010). Water repellency on wood surfaces persisted for 8 weeks. After 12 months of weathering, specimens treated with 1% nanoZn presented approximately 10% of reduction in 24 h water absorption, while specimens treated with 2.5 and 5.0% nanoZn showed 32% reduction in 24 h water absorption, when compared to untreated samples (Clausen et al., 2010). The Water absorption changes founded are an important result because in imply in a decreasing of equilibrium moisture content of the wood; It is known that in moisture contents below the fiber saturation point natural resistance of wood to insects and fungi increase (Lepage et al., 2017).

Authors concluded that nanoZnO has desirable wood protection properties, such as leach resistance, UV protection, and termite resistance, even it would provide no adequate protection against decay or mold (Clausen et al., 2009).

In general, nanotechnologies have the potential to affect all wood preservation field through the development of new preservatives with low toxicity and high effectiveness. Nanotechnologies also can affect wood protection on several parameters as penetration, retention, and leaching. The next sections will discuss it.

PENETRATION OF NPS IN THE WOOD

According to Freeman and McIntyre (2008), the size of metal particles may affect penetration of the wood cell walls and reactions with wood molecular constituents. The degree of penetration and uniformity of distribution of particles into wood cellular structure is inversely related to the prevalence of large size particles.

Large particles may obstruct tracheids and inhibit the preservative penetration. On the other hand, complete penetration and uniform distribution of preservative in wood is expected if the particle size of the preservative is smaller than the diameter of the window pit (10nm) or membrane openings in a bordered pit (400 – 600 nm). In concern to hardwoods, wood pore diameters are measured in micrometers. A Diameter of 50 μm is considered a relatively small pore size (Maier, 2018) however it is greater than bordered pit of softwoods.

NPs are created with controlled particle size and some of them demonstrated high dispersion stability (Freeman and McIntyre, 2008), being this an important feature, since particles-size in the range of 1-100 nm may improve penetrability of chemical reagents into the

wood (Freeman and McIntyre, 2008; Kartal et al., 2009). Nanometal preparations have low viscosity and a surfactant addition can further increase dispersion stability by enabling liquid dispersion of higher concentrations of nanometal particles (Kartal et al., 2009; Lykidis et al., 2013). Information about nanoTiO₂ penetration into the microscopic pores of wood are poorly reported. NPs penetration depth can be estimate by SEM analysis. It was described as a thin homogeneous layer of TiO₂ NPs, with an average size of 50 nm covering wood internal structures, without changing natural appearance (De Filpo et al., 2013).

Regarding to wood protection requirements, nanometals show potential for great penetration and protection, with a more uniform particulate distribution over a wood surface.

CHEMICAL RETENTION IN THE WOOD

Retention is the amount of preservative that is retained in the sapwood after a treatment cycle. It is one measurement of the degree of protection provided by a treatment, been usually expressed as kilograms of preservative per cubic meter of wood (Canadian Wood Council, 2018). Specimen size and configuration cause differences in chemical retention (Kartal et al., 2009; Mantanis et al., 2014). Thin specimens had higher retention than large ones (Kartal et al., 2009).

Comparing NPs with microparticles, there was no difference between nanoB and H₃BO₃ chemical retentions, however, chemical retention of NanoCu was 30% less than CuSO₄. For nanoZn preparations (30 nm, without surfactant) and ZnSO₄, retentions were similar (Kartal et al., 2009). Otherwise, nanoZnO as aqueous dispersions (with 30 nm and 70 nm average diameters) presented higher chemical retentions than ZnSO₄ treated wood, for the same concentration (Clausen et al., 2011).

Surfactants affect chemical retention (Kartal et al., 2009; Mantanis et al., 2014). With surfactant, retentions were 30% and 16% lower than ZnSO₄, for nanoZn and nanoZn with Ag, respectively (Kartal et al., 2009), and the highest retention levels in treatments with nanoZnO were obtained without acrylic emulsion (Mantanis et al., 2014).

Due to differences that specimen sizes, emulsions and emulsifying agents cause to chemical retention of wood preservatives, it is hard to compare reported results. However, great development can be achieved by exploring these features.

CHEMICAL LEACHING OF THE NPS

Wood preservatives have to present ability to fixate inside wood. This parameter is usually expressed

through leaching rates. Leaching is greatest in treatments with high retention levels and high exposed surface area. The highest rates of leaching occurs within the first months of service, and it is increased by exposing the wood to water flow, low pH, and water-soluble organic acids (Lebow, 1996).

Information provided over depletion of chemical retention of nanoZnO (30 nm) on wood weathered specimens (12 months of outdoor exposure) suggested specimens vacuum treated with 1% of nanoZnO were leach resistant, while ZnSO₄ readily leached (Clausen et al., 2010). It happens because ZnSO₄ leached faster than nanoZn (Kartal et al., 2009). NanoZnO retention in specimens treated with 1% nanoZnO presented no changes, but specimens treated with 2.5 and 5.0% nanoZnO showed 65 and 58% of nanoZnO loss, respectively (Clausen et al., 2010).

Leaching from wood treated with nanoCu (30 nm particle diameter) was barely detectable, but the rate of leaching for CuSO₄ was faster. On the same way, nano preparations of Zn and Zn with Ag showed lower leaching than ZnSO₄ (Kartal et al., 2009). NanoB presented very low leaching resistance (Mantanis et al., 2014; Lykidis et al., 2013; Kartal et al., 2009). Van der Waals forces and changes in charge can explain the low leaching of nanometals (Kartal et al., 2009; Clausen et al., 2009; Clausen et al. 2010).

NanoCuO treated specimens with and without emulsion showed low percentage of leaching (Mantanis et al., 2014; Clausen et al., 2009). Specimens treated with nanoCu, with and without surfactant, had high leaching resistance compared to the control CuSO₄. NanoZn and nanoZn plus Ag, both with surfactant, had low percentage of leaching (9% and 8%, respectively), when compared to Zn preparations without surfactant (31% and 33%), and ZnSO₄ (84%) (Kartal et al., 2009). Preparations of nanoZnO and zinc borate plus acrylic emulsion had a lower percentage of leaching than the same zinc preparations without emulsion. However, nanoCuO treated specimens without emulsion had the lowest percentage of leaching (7.5%), while nanCuO with emulsions had high percentage of leaching, 13% and 29%, respectively (Mantanis et al., 2014). It happens because addition of a water-borne acrylic emulsion binder in the compound may increase its affinity to wood polymers and subsequently decrease leaching (Lykidis et al., 2013).

It is possible to affirm that leaching can be controlled by using emulsions and surfactants (Kartal et al., 2009; Lykidis et al., 2013; Mantanis et al., 2014), but this affirmation has to be more explored in future researches, looking for improved results.

CONTROL OF RELEASING OF BIOCIDES

In order to control releasing, extend wood preservatives activity, and reduce their toxic effects, biocides NPs could be encapsulated. Encapsulation provides controlled means of prolonging biocidal activity, protecting against biocide leaching, UV-induced degradation, and consequently increasing lifetime effects (Sørensen et al., 2010). Besides, external conditions such as the pH, can be used for a controlled releasing when they reach specific required conditions (Pérez-de-Luque and Rubiales, 2009).

Controlled release of chemical substances can be evaluated by using different approaches. The surface assembly of polyelectrolyte multilayers on the microcapsule surface is a very promising tool for controlling the release of hydrophobic actives (Trojer et al., 2015).

Studies demonstrated the effectiveness of an environmentally friendly sustained releasing system of fipronil insecticide into silica nanocapsules against subterranean termites in laboratory tests (Wibowo et al., 2014). Polymeric capsules containing biocides improved the resistance of birch wood to white-rot attack, with a very low biocide loading required (0.1 to 0.8 Kg·m⁻³). In general, nature-derived material, as carbon nanotubes, polymers, mesoporous alumina and mesoporous/hollow silica present high potential for controlled release systems, according to several authors (Mattos et al., 2017).

Even if studies about NPs control of releasing are still incipient, they are very promisors because they could increase effectiveness of wood preservatives, and consequently decrease costs of maintenance and replacement of wood products.

HUMAN AND ENVIRONMENTAL RISKS OF NPS

The increasing usage of engineered NPs intensify the probability of consumer and workers to get into contact with materials that might cause adverse health effects (Oberdorster et al., 2005; Silva et al., 2010). Despite this, there are few information about NPs safety.

The exponential developments of nanotechnologies contrast to concerns of public health, due to the insufficient risk assessment to environment and human health (Louro et al., 2013). Both beneficial (e.g. photocatalytic activity and water repellence) or harmful effects (e.g. induction of oxidative stress and cellular dysfunction) can be exerted by the desired properties of engineered NPs (Stoeger et al., 2009).

Künniger et al. (2013), studying functionality and environmental impacts of metallic NPs of Ag, found

the total Ag released from products with nanoAg was proportional to the overall erosion of the coating, and there was indication that metallic nanoAg are transformed to Ag complexes less toxic than ionic Ag. NanoCu-based wood treatments may end up dispersed into the environment being inhaled, causing harm, and become a human health potential risk (Civardi et al., 2015b). It is advocated to intensify studies focused at a complete characterization of its toxicity and behavior in environmentally exposure (Anjum et al., 2015).

NPs of TiO₂ may undergo to physicochemical transformation during incineration, requiring further research to identify what NPs will be emitted to the environment from incinerated material (Massari et al., 2014). Engineered NPs from Ag had higher ecotoxic impact than those from TiO₂, with a linear regression between Ag content in products and the potential ecotoxicity impacts to environment (Miseljic and Olsen, 2014). Kaiser et al. (2013b), working about engineered NPs used at paint industry showed that neither the gastrointestinal cells nor immune system cells were significantly affected when exposed to nanoTiO₂ and nanoSiO₂, while several cell parameters were affected when exposed to nanoAg. Future research aiming at unveiling the destination of nanoAg particles, its transformation, accumulation, and toxicity potential, as well as their impact on environmental and human health are recommended (Anjum et al., 2013).

NanoZnO has been indicated as a promising antibacterial, antifungal, and antiviral agent (Beegam et al., 2016) with promising results in the control of several kinds of cancer cells (Rasmussen et al., 2010; Wahab et al., 2013a; Wahab et al., 2013b; Selvakumari et al., 2015; Vinardell and Mitjans, 2015; Namvar et al., 2015; Bisht and Rayamajhi, 2016). Studies have also shown potential beneficial environment effects of nanoZnO (Beegam et al., 2016), but in order to understand their potential risk, a comprehensive material life cycle analysis is necessary (Bystrzejewska-Piotrowska et al., 2009; Oliveira et al., 2012; Silva et al., 2012a; Silva et al., 2012b).

Due to the increasing concern of NPs security, there is a deceleration in nanotechnology research, in the field of medical and food industries, because of the fact that researchers have found that NPs could diffuse into the human body and cause adverse effects. Considering the increasing of production and application of nanomaterials, as well as, the related consumer products, it was suggest that a testing strategy for different kinds of NPs have to be established (Hougaard et al., 2015). Society might overestimate the short-term effects of nanotechnologies, while underestimating the long-

term effects (Bystrzejewska-Piotrowska et al., 2009). Despite this, many authors regard nanotechnology as the base for the next industrial revolution (Resch and Farina, 2015).

PROSPECTS AND CONSIDERATIONS ON WOOD PROTECTION

There are many possibilities of nanotechnologies applications on wood protection. Nanometals-based treatments present good perspective to control water repellence, scratch resistance, durability, self-cleaning surfaces, wood biodegradation, and also can improve weathering resistance.

White-rot fungi inhibition and termites control by using NPs were reported; but no nanometal preparation were effective against brown-rot fungi – *Meruliporia incrassata*, *Gloeophyllum trabeum* and *Tyromyces palustris*. However, control over decay caused by *Mucor circinelloides* were reported.

Authors reported information about chemical retention and leaching of NPs and weathering protection through NPs, with good results. No significant differences between different NPs sizes were reported for leach resistance and termites. However, some NPs can be considered as friendly biocides with potential application on wood protection industrial process in the future, as nanoZnO and nanoTiO₂.

NPs-based wood preservatives have to be properly explored in future researches, focusing on the most promising results reported, as well as, other chemical substances with biocides activity, exploring the nanotechnology open issues. It is necessary to keep in mind that there are not sufficient risk assessment for human health and the environment impacts of NPs yet. However, although there is no answer to all questions, based on this review, it can be considered that NPs-based treatments may perform an important role on the next generation of wood protection.

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